Aluminium Evaporation During Ceramic Crucible Induction Melting of Titanium Aluminides

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Abstract. Melting TiAl based alloys in ceramic crucibles often leads to chemical contamination, alloy heterogeneity and non-metallic inclusions. The severity of such phenomena usually depends on the nature of crucible materials, the melting stock composition and the melting parameters, namely superheating time and temperature and melting pressure. Among the referred drawbacks, Al loss during melting is a critical aspect, as its concentration in TiAl based alloys has a very strong effect in their mechanical properties. Although a few studies of critical factors affecting the evaporation behaviour of Al during electron beam and induction skull melting of Ti-Al alloys had been carried out, until now no information was released on this subject for the ceramic crucible induction melting process.

In this work a Ti-48Al alloy was induction melted in a zircon crucible with Y_2O_3 inner layer, using 50 and 100 ºC superheating temperatures and 0, 60 and 90 second holding times, and poured into a graphite mould. The effect of different temperature/time combinations in the alloy composition, Al loss by evaporation and extent of the metal/crucible interaction was studied for different melting pressures.

Al loss was found to increase significantly for melting pressures below around 10^{-1} mbar, at a rate that increases as melting pressure decreases, until a maximum rate is reached, remaining constant for lower pressure levels. Metal/crucible interaction increased directly with the melting pressure and superheating time, leading to alloy contamination with yttrium and oxygen. For the experimental set-up and conditions used on this work, optimal superheating time/pressure combinations that lead to acceptable alloy composition and sanity have been identified.

Introduction

The traditional route to cast titanium parts is the combination of the induction skull melting process (ISM) with the investment casting process and using centrifugal pouring. However, ISM has a high impact in the castings final cost and generates high levels of rejections, mainly due to the difficulty to reach suitable superheating. To overcome this problem, excessively high mould preheat temperatures are frequently used, thus increasing the probability of a metal-mould reaction occurring leading to metal contamination, and development of solidification defects. The current solution to overcome such drawbacks it to increase the section thickness of the castings for subsequent machining, but this solution adds further costs and eliminates the potential benefits of near net shape casting.

During the last years, some of the authors developed extensive research on this field, mainly focusing the development of a suitable ceramic crucible for the traditional vacuum induction melting process. As a result, a $ZrO_2.SiO_2$ based crucible with inner Y_2O_3 layer has been developed and patented. Melts conducted in those crucibles revealed the lowest oxygen contamination referred so far for ceramic crucible melting of TiAl [1].

Due to the high reactivity of Ti based alloys, melting and pouring have to run under vacuum or inert gas atmosphere. Nevertheless, vacuum melting can be detrimental to the chemical composition accuracy of some alloys. Depending on the vacuum level in the melting chamber, loss by

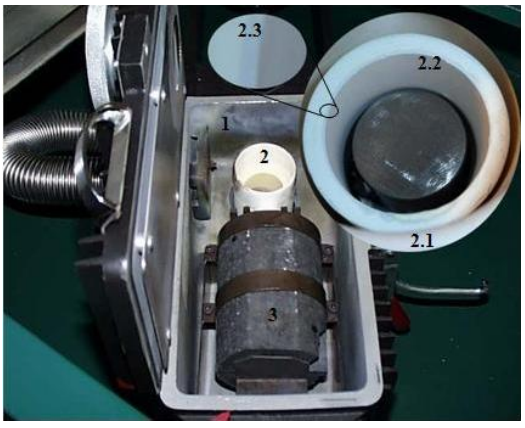
evaporation of elements with high vapor pressure can be very significant. This aspect is particularly important when melting Ti-Al based alloys due to the high vapor pressure of Al, which is 300 times higher than Ti in TiAl melts [2], and its low melting temperature when compared with Ti. Depending on the vacuum pressure and the melting technique Al loss by evaporation in TiAl melts can reach 15wt% [3], which is extremely relevant since the microstructure and mechanical properties of TiAl alloys are very sensitive to the Al content [4]. On the other hand, if melting is performed in ceramic crucibles at higher pressure, metal-crucible reactivity may increase, and metal contamination will occur. Thus, when using this melting technique to produce TiAl based alloys, a suitable equilibrium between pressure and superheating parameters has to be carefully established to avoid alloy contamination with elements from the crucible material and/or excessive aluminum loss. Although some theoretical models have been developed to describe Al evaporation in TiAl melts during ISM [2,3], their applicability to ceramic crucible induction melting is not known.

Moreover, due to the inherent poor thermal shock resistance of ceramic crucibles, heating rates are necessarily low, increasing the melting time, thus the extension of a possible metal-crucible interaction, as well as the amount of Al loss. Therefore, on a first approach, melting pressure must be kept as low as possible to avoid metal contamination, without inducing excessive Al evaporation, meaning that an ideal pressure level has to be identified.

In this work different combinations of melting pressure and superheating temperature and time were tested and characterized concerning its influence in the chemical composition and microstructure of Ti-48Al alloys.

Experimental procedure

Melting charges weighing 1.3×10^{-1} kg were prepared from CP Ti rod (with 0.23wt% O) and Al fragments and melted in a Linn Hightherm 700 VAC ceramic crucible induction melting furnace. The melting crucibles were home-made zircon ($ZrO_2.SiO_2$) based crucibles with inner dimensions Ø40mm × 80 mm with a 200 μm thick inner Y_2O_3 layer. The average crucibles porosity was 35±3%, evaluated according to the ISO Standard 5017:1998 (E). The average surface porosity of the Y_2O_3 coatings was 14±2%, evaluated by digital imaging techniques, using Image Pro plus software. The melting crucible was positioned inside a home-made $ZrO_2.SiO_2$ pouring crucible with lip (Fig. 1). A graphite mould with Ø20 × 120 mm cylindrical cavity was used to pour the molten alloys, in order to insure that oxygen pickup would result exclusively from the metal-crucible interaction during the melting operation.



1. Furnace
2. Crucible set
   - 2.1 Pouring crucible
   - 2.2 Melting crucible
   - 2.3 Y_2O_3 layer

Figure 1 - Experimental set-up and positioning of the melting stock inside the crucible

Melting was performed in vacuum or under a controlled atmosphere of commercially pure dry argon. Before the heating cycle, the chamber was evacuated down to 10^{-3} mbar and back-filled with argon five times, in order to reduce the oxygen content to a minimum level, and then the chamber pressure was adjusted for the desired value. Heating was always performed at constant power and

the alloy that was forming remained on a mushy state due to the dissolution of titanium in aluminium, which gradually raised the melting temperature of the alloy. Around 15 minutes after starting of the heating cycle, temperature reached 1500±10ºC and the first liquid metal became visible. Melts were then maintained at the selected temperatures (1550 and 1600ºC) for 60 and 90 seconds for homogenization and centrifugally poured at 400 rpm, with an acceleration of approximately 25g, into the graphite mould. For the sake of comparison, samples were also poured immediately after reaching the selected superheating temperatures. Temperature was controlled with a type B thermocouple, protected by Mo-Al_2O_3-ZrO_2 refractory sheath. Table 1 presents the melting variables combinations used in this work.

Table 1 - Chamber pressure and superheating temperature and time

Melt #	Temperature [ºC]	Time [s]	Pressure [mbar]
1-48	1550, 1600	0, 60, 90	0.005 / 0.01 / 0.02 / 0.05 / 0.1 / 0.15 / 0.5 / 1

Samples for characterization were collected from the middle of the cast cylinders by sectioning them at 50% of their height. Phase identification and chemical composition were performed by quantitative EDS analysis with standards of pure Ti, Al, and Y using a high-resolution FEI Quanta 400 FEG E Scanning Electron Microscope coupled to an EDAX Genesis X4M X-Ray Energy Dispersive Electron Spectrometer. The error associated to Ti and Al measurements was 0.2 at.% and the error of Y measurement was 0.03 at.%. Overall oxygen content was measured by the IGF technique (Inert Gas Fusion) on a Lecco TC-136 analyser, with an associated error of 20 ppm.

Results and Discussion

The as-cast microstructure of every sample was fully lamellar with two phases - $\alpha_2 + \gamma$, which is the typical microstructure of as-cast γ-TiAl alloys with Al content around 48 at%, when the cooling rates between 0.2 and 1ºCs^{-1} are used, as it happened in this work. The microstructure at the surface of the cast samples was not affected by the pouring temperature or the chamber pressure. Although it could be expected that the high reactivity of titanium with carbon would have led to the formation of TiC, it seems that the reaction did not occur, which may have been a consequence of the high cooling rate that decreased the reaction kinetics.

In every cast sample smoke started to escape from the melting crucible, condensing as a light grey powder on the furnace glass window, at a temperature slightly below that corresponding to the first visible liquid metal (1500±10 K). The amount of powder condensing at the furnace window increased with increasing superheating time and temperature, and it was particularly important when the pressure inside the chamber was below 0.01 mbar. An EDS analysis revealed that condensed powder was basically pure aluminium that evaporated during melting, confirming the findings of other authors for ISM [2]. On Table 2 the final Al content of the theoretical Ti-48Al alloys is presented for different superheating time/temperature/chamber pressure combinations. In Fig.2 the correspondent Al loss was plotted against the melting pressure and it is clear it increases significantly with the superheating parameters and decreasing chamber pressures. For 1550ºC, Al loss was almost negligible for melting pressures above 0.1 mbar for both superheating times. For lower pressure values, it increased gradually as the chamber pressure dropped and superheating time increased, until reaching a maximum value of 2.4 at% for 90 seconds at 0.005 mbar. A similar behaviour occurred for 1600ºC, but in this case Al loss started increasing at 0.15 mbar and reached a maximum value of 3.45 at% for 90 seconds at 0.01 mbar. It is also clear that Al evaporation was also proportional to the interval of time that the alloy was in the liquid state.

Values presented in Table 2 were converted to Al loss/time unit, and the results are shown in Fig.3 as the variation of Al loss rate with the chamber pressure and superheating temperature. Two threshold level pressures are clearly identified, corresponding to a *critical pressure* (*Pc*) below which the Al evaporation rate becomes constant, and an *impeding pressure* (*Pi*) above which no

significant Al evaporation occurs. Between those two values, Al loss rate changes very fast. *Pc* was the same for both superheating temperatures (0.01 mbar) but the *Pi* was 0.1 mbar for 1550ºC and increased to 0.15 for 1600ºC, which considerably agrees with the theoretical model developed for TiAl ISM [2,3] both in the curves qualitative trend and the experimental pressure results. For a Ti-45Al alloy obtained by the ISM process, Jingjie et al [2] report *Pc* values between 0.01 and 0.015 mbar, and *Pi* between 0.15 and 0.20 mbar for melting temperatures between 1550 and 1600ºC. These findings reveal that the theoretical model developed for ISM can be successfully applied to anticipate the critical and impeding melting pressures of Al evaporation on the ceramic crucible induction melting of Ti-48Al. However, since the evaporation mass-transfer depends on the area of evaporation (thus the diameter of the melting crucible) [2,3], the absolute values of Al evaporation rates obtained on this work are only valid for the crucible size that has been used.

Table 2 - Final Al content (at%) of induction melted Ti-48Al alloys for different superheating parameters, at different melting chamber pressures

Temperature	Time	Melting chamber pressure (mbar)							
(ºC)	(s)	0.005	0.01	0.02	0.05	0.1	0.15	0.5	1
1550	0	47.40	47.40	47.50	47.55	47.78	47.80	47.80	47.85
1550	60	46.20	46.26	46.72	47.37	47.73	47.75	47.76	47.77
1550	90	45.60	45.69	46.33	47.28	47.70	47.73	47.75	47.75
1600	0	47.25	47.25	47.42	47.60	47.70	47.80	47.80	47.85
1600	60	45.40	45.45	46.22	46.90	47.45	47.70	47.75	47.76
1600	90	44.55	44.55	45.53	46.60	47.30	47.64	47.67	47.70

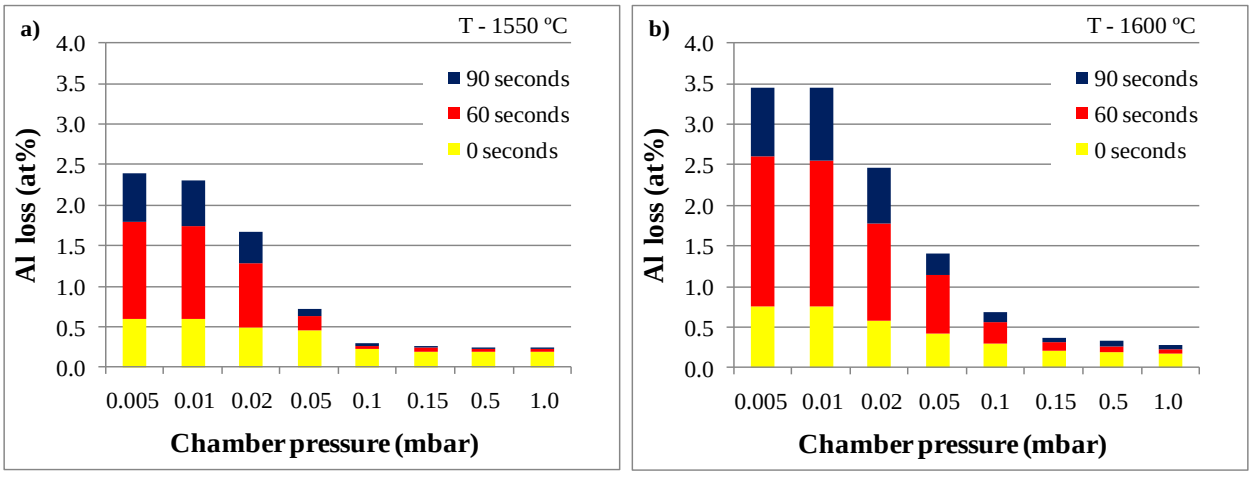


Figure 2 - Al loss in ceramic crucible induction melted Ti-48Al alloys as a function of superheating time at a) 1550ºC and b) 1600ºC, for different melting chamber pressures

Every cast sample was found to be contaminated with oxygen (Table 3), whose concentration was higher than that attributed to the oxygen present on the components of the melting stocks (0.16 wt% max), revealing that *"oxygen enrichment"* has occurred. Since oxygen pick-up from the atmosphere can be excluded, the only possible source of oxygen was the crucible material, which means that some sort of interaction occurred between the Y_2O_3 layer of the melting crucible and the cast alloys. According to its free energy of formation, Y_2O_3 is thermodynamically much more stable than titanium and aluminium oxides, thus no reaction of the crucible inner layer with the cast alloy should be expected. Thus, the most probable cause is the dissolution of the Y_2O_3 layer by the metal, that confirms previous results of some of the authors [1] and other researchers [5]. Moreover, the presence of a residual content of yttrium in solution (maximum contamination of 0.08 at% for 1600ºC/90 seconds/0.5 and 0.1 mbar) is a strong indicator that dissolution has occurred.

For each combination temperature/superheating time oxygen enrichment increased with the melting pressure, and that increase became higher as the temperature and superheating time raised [see Table 3 – column (Max – Min)]. This means that the effect of the melting pressure in the oxygen enrichment is more evident for higher temperatures and superheating times. On the other hand, for the same chamber pressure, oxygen enrichment increased with both the melting temperature and superheating time, with the maximum contamination (0.051 wt%) corresponding to the highest pressure and superheating parameters (1600ºC/90 second/1 mbar), and the increase being higher for the highest chamber pressures (see table 3 – lines Difference 90s-0s).

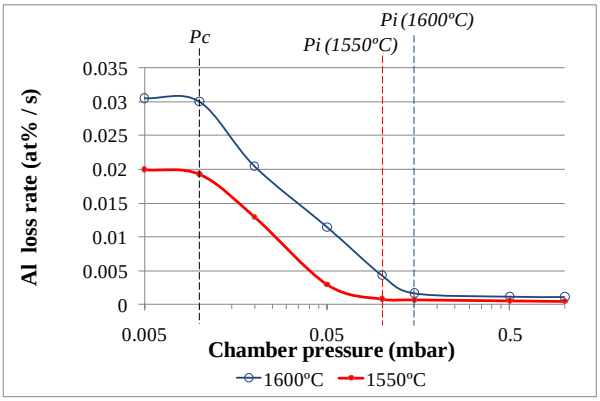


Figure 3 - Al loss rate (at%/s) in ceramic crucible induction melted Ti-48Al alloys as a function of melting chamber pressure and melt temperature

Table 3 - Oxygen enrichment during ceramic crucible induction melting of Ti-48Al alloys, for different processing conditions

Temperature	Time	Melting pressure [mbar]								
[ºC]	[s]	0.005	0.01	0.02	0.05	0.1	0.15	0.5	1	Máx - Min
1550	0	0.020	0.022	0.022	0.024	0.024	0.028	0.027	0.029	0.009
1550	60	0.023	0.025	0.025	0.029	0.027	0.032	0.036	0.037	0.014
1550	90	0.023	0.028	0.027	0.034	0.036	0.045	0.038	0.043	0.020
Dif. (90 s –0 s)		0.003	0.006	0.005	0.010	0.012	0.017	0.011	0.016	
1600	0	0.020	0.023	0.023	0.026	0.027	0.030	0.033	0.032	0.013
1600	60	0.025	0.026	0.025	0.038	0.040	0.039	0.041	0.042	0.017
1600	90	0.027	0.028	0.027	0.041	0.045	0.050	0.051	0.051	0.024
Dif. (90 s – 0 s)		0.007	0.005	0.004	0.015	0.018	0.020	0.018	0.019	

The results of this work suggest that the processing parameters of ceramic crucible induction melting of Ti-Al alloys must be carefully selected, in order to fulfill the binomial Al evaporation / residual contamination, bearing in mind the envisaged alloy composition and the casting requirements. In TiAl based alloys with Al content close to 48 at%, oxygen must be kept as low as possible to avoid embrittlement. Nevertheless, for many applications, oxygen contents up to 0.05 wt% are still accepted, since the alloys keep a minimal elongation of 0.5% and no changes in tensile strength are expected for oxygen contents below 0.1 wt% [6]. In what concerns to Al content, a decrease of 1.5 at% Al has no effect in the fracture strength of the alloy, and causes an elongation decrease of about 0.1% [4].

On Figure 4, Al loss and O enrichment are plotted as a function of melting chamber pressure for the temperature/superheating time combinations used on this work. The shadowed areas correspond to those processing conditions that will lead to less than 0.045 wt% O enrichment (we assume that in most industrial melting processes O content of the melting stocks is less than 0.010 wt%) and to Al loss lower than 1.5 at%, for the experimental conditions and set-up used in this work. Although this is a lab scale approach, a similar exercise can be done for a specific industrial plant, as far as the effects of the melting variables in the alloys compositions are known, as well as the castings

requirements. This exercise will help to select the most suitable processing conditions and melting stock composition for a specific application, taking into account its alloy composition requirements and the casting geometry and dimensions.

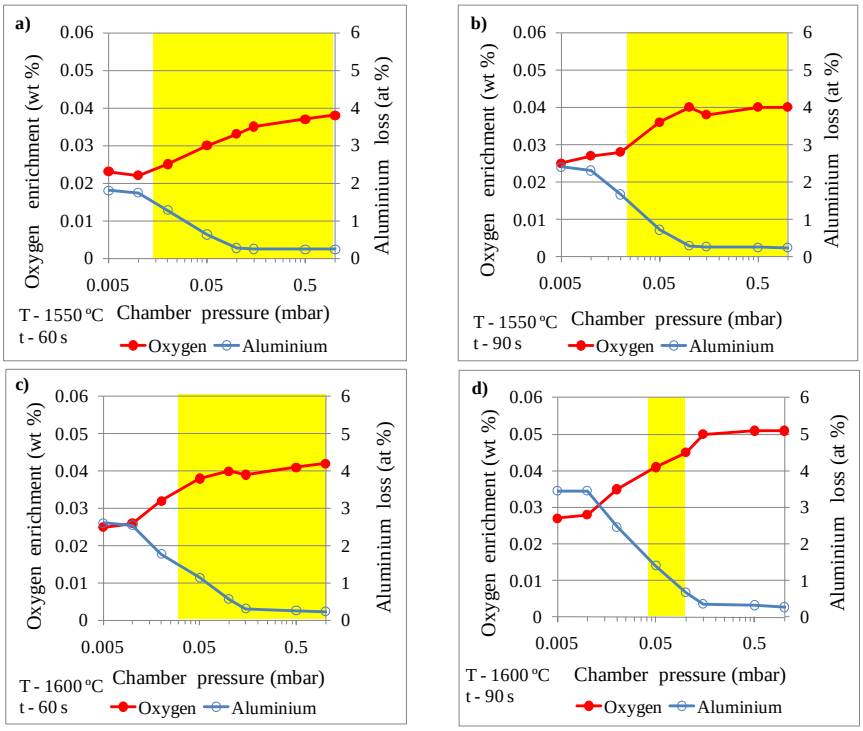


Figure 4 - Variation of Al and O contents in ceramic crucible induction melted Ti-48Al alloys as a function of the melting pressure and

Conclusions

The theoretical models available to preview the Al loss dynamics in the ISM of Ti-48Al alloys can be successfully applied to ceramic crucible induction melting. Al loss can reach 3.45 at% if pressures between 0.01 and 0.005 mbar are used simultaneously with 1600ºC casting temperature and 90 second superheating time. The Al loss rate is constant for pressures below 0.01 mbar for 1550 and 1600ºC and above 0.1 or 0.15 mbar for 1550 and 1600ºC, respectively.
The melting pressure was found to affect the extension of metal-crucible interaction and to promote oxygen contamination of the cast alloys, which increases directly with the pressure.
For each temperature/time combination an optimum pressure range was identified to simultaneously reduce the Al loss to a max. of 1.5 at% and to limit oxygen contamination to a max. of 0.045 wt%.

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